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(71) 出願人 000005887

三井化学株式会社
東京都千代田区霞が関三丁目2番5号

(72) 発明者 広 瀬 敏 行

山口県玖珂郡和木町和木六丁目1番2号
三井化学株式会社内

(72) 発明者 山 本 陽 造

山口県玖珂郡和木町和木六丁目1番2号
三井化学株式会社内

(74) 代理人 弁理士 鈴木 俊一郎

(54) 【発明の名称】 環状オレフィン系樹脂成形体のスチームまたは熱水処理方法

(57) 【要約】

【課題】環状オレフィン系樹脂成形体を白化させることなくスチームまたは熱水により滅菌処理することができる環状オレフィン系樹脂成形体のスチームまたは熱水処理方法を提供する。

【解決手段】サーマルメカニカルアナライザーで測定される軟化点温度が110℃以上である環状オレフィン系樹脂からなる成形体を、スチーム処理または熱水処理した直後に、該処理温度をT℃とするとき(T-50)℃よりも高い温度で、かつ相対湿度50%以下の雰囲気中に10分以上保持する。上記環状オレフィン系樹脂は、エチレンと環状オレフィンとのランダム共重合体であることが好ましい。

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Jun 8, 1999

DERWENT-ACC-NO: 1999-389443

DERWENT-WEEK: 199936

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TITLE: Steam processing of resin mold for medical, pharmaceutical application - involves processing the mold at a particular temperature by steam and maintaining it in an atmosphere of specific relative humidity

PATENT-ASSIGNEE:

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CODE

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JP 11152355 A

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INT-CL (IPC): B29 C 71/02; B29 K 23:00; C08 F 210/02; C08 J 7/00

ABSTRACTED-PUB-NO: JP 11152355A

BASIC-ABSTRACT:

NOVELTY - The mold made of cyclic olefin group resin (softening temperature measured by thermal mechanical analyzer is above 110 deg. C) is processed at a temperature T c by steam or hot water. The mold after processing is maintained at a temperature of (T-50) deg. C or more in an atmosphere of relative humidity 50 % or less.

USE - Used as medical, pharmaceutical tools for medical, pharmaceutical applications.

ADVANTAGE - The mold is sterilized by steam without producing a whitening and the haze was retained even after processing.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: STEAM PROCESS RESIN MEDICAL PHARMACEUTICAL APPLY PROCESS TEMPERATURE
STEAM MAINTAIN ATMOSPHERE SPECIFIC RELATIVE HUMIDITY

DERWENT-CLASS: A17 A96 B07

CPI-CODES: A04-G; A11-C; A12-H05; B04-C03B;

CHEMICAL-CODES:

Chemical Indexing M1 *01*

Fragmentation Code

G000 G622 G810 M280 M320 M415 M423 M424 M510 M520
M530 M541 M610 M720 M740 M903 M904 N104 N513 Q110
Q120 V743

Ring Index

04063

Markush Compounds

199933-CAT01-P 199933-CAT01-Q

Chemical Indexing M1 *02*

Fragmentation Code

H7 H721 M210 M212 M320 M416 M423 M424 M610 M720
M740 M903 M904 M910 N104 N513 Q110 Q120 V743

Specific Compounds

00326P 00326Q

Registry Numbers

0326P 0326S

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0326P; 0326S

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1] 018 ; G0033*R G0022 D01 D02 D51 D53 ; R00326 G0044 G0033 G0022 D01 D02
D12 D10 D51 D53 D58 D82 ; H0011*R ; H0113 H0011 ; P1150 Polymer Index [1.2] 018 ; ND07 ; N9999
N6871 N6655 ; Q9999 Q7932 Q7885 ; Q9999 Q7987*R ; B9999 B4273 B4240 ; B9999 B4295 B4240 ;
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SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1999-114945

DERWENT-ACC-NO: 1999-389443

DERWENT-WEEK: 199936

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TITLE: Steam processing of resin mold for medical,
pharmaceutical application - involves processing
the mold at a particular temperature by steam and
maintaining it in an atmosphere of specific relative humidity

----- KWIC -----

Basic Abstract Text - ABTX (1):

NOVELTY - The mold made of cyclic olefin group resin (softening
temperature measured by thermal mechanical analyzer is above 110 deg. C) is
processed at a temperature T c by steam or hot water. The mold after processing is
maintained at a temperature of (T-50) deg. C or more in an atmosphere of relative
humidity 50 % or less.

Basic Abstract Text - ABTX (3):

ADVANTAGE - The mold is sterilized by steam without producing a
whitening and the haze was retained even after processing.

Title - TIX (1):

Steam processing of resin mold for medical, pharmaceutical
application - involves processing the mold at a particular temperature by steam and
maintaining it in an atmosphere of specific relative humidity

Standard Title Terms - TTX (1):

STEAM PROCESS RESIN MEDICAL PHARMACEUTICAL APPLY PROCESS TEMPERATURE
STEAM
MAINTAIN ATMOSPHERE SPECIFIC RELATIVE HUMIDITY

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CLAIMS

[Claim(s)]

[Claim 1] The steam or the hot water art of an annular olefin system resin Plastic solid which is temperature higher than ** when the aforementioned processing temperature is made into T degrees C immediately after steam-processing or hot water processing the Plastic solid which the softening temperature temperature measured with a thermal mechanical analyzer becomes from the annular olefin system resin which is 110 degrees C or more (T-50), and is characterized by holding 10 minutes or more in the atmosphere of 50% or less of relative humidity.

[Claim 2] The steam or the hot water art of an annular olefin system resin Plastic solid according to claim 1 to which the aforementioned annular olefin system resin is characterized by being the random copolymer of ethylene and an annular olefin.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the steam or the hot water art of an annular olefin system resin Plastic solid which can carry out sterilization processing by steam or hot water, without making an annular olefin system resin Plastic solid milk.

[0002]

[Background of the Invention] A polyolefine is non-toxicity, and is excellent in transparency, has properties, such as a thermoforming plain-gauze cone, and is used for the use more extensive than before. if compared with alpha olefins, such as ethylene and a propylene, also among such polyolefines -- ** -- the annular olefin system resin obtained from the annular olefin which has high structure is excellent in transparency, thermal resistance, rigidity, dampproofing, etc. compared with polyethylene, polypropylene, etc., and use for various uses is studied

[0003] Especially this annular olefin system resin also has the property that the sterilization processing by steam or hot water is possible, and is suitable as molding materials, such as medical treatment and medicine tools which perform such sterilization processing, or a food-grade container.

[0004] However, the Plastic solid which consists of this annular olefin system resin has the trouble that milkiess (cloudiness) may be produced in a Plastic solid and transparency may fall to it, when steam or hot water performs sterilization processing.

[0005] Although how to include the additive for preventing a white blush mark for example, in an annular olefin system resin Plastic solid as the solution method of such a trouble etc. can be considered, as for especially the Plastic solid used for medical treatment and a medicine use, it is desirable not to include an additive etc. as much as possible.

[0006] For this reason, an art by the steam or hot water of an annular olefin system resin Plastic solid which can perform sterilization processing by steam or hot water was desired, without producing a white blush mark, even if it did not include the additive for milkiess prevention etc. in an annular olefin system resin Plastic solid.

[0007]

[Objects of the Invention] this invention is made in view of the above conventional technology, and it aims at offering the steam or the hot water art of an annular olefin system resin Plastic solid which can carry out sterilization processing by steam or hot water, without making an annular olefin system resin Plastic solid milk.

[0008]

[Summary of the Invention] When the steam or the hot water art of an annular olefin system resin Plastic solid concerning this invention makes this processing temperature T degrees C immediately after steam-processing or hot water processing the Plastic solid which the softening temperature temperature measured with a thermal mechanical analyzer becomes from the annular olefin system resin which is 110 degrees C or more (T-50) It is temperature higher than **, and is characterized by holding 10 minutes or more in the atmosphere of 50% or less of relative humidity. As for the above-mentioned annular olefin system resin, it is desirable that it is the random copolymer of ethylene and an annular olefin.

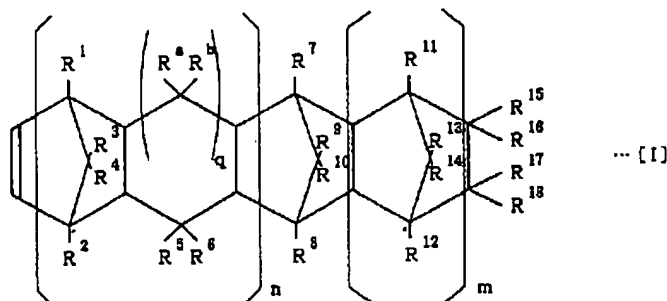
[0009]

[Detailed Description of the Invention] The steam or the hot water art of an annular olefin system resin Plastic solid which starts this invention below is explained concretely. In the steam or the hot water art of an annular olefin system resin Plastic solid concerning this invention, the Plastic solid which consists of an annular olefin system resin is steam-processed or hot water processed by method which is mentioned later.

[0010] Although the annular olefin system resin whose softening temperature temperature measured with a thermal mechanical analyzer is 110 degrees C or more is used in this invention, this annular olefin system resin is obtained from the annular olefin shown by the following formula [I] or [II]. This annular olefin is explained first.

[0011]

[Formula 1]

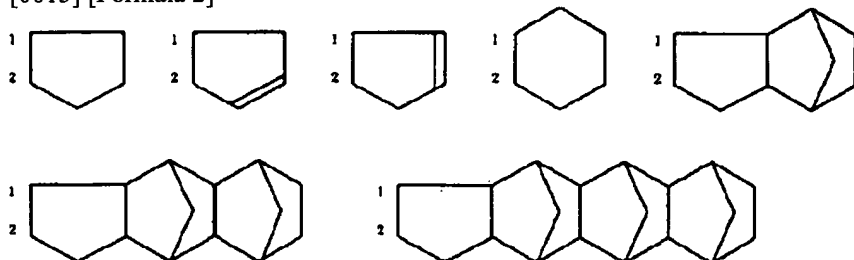


[0012] n is 0 or 1 among the above-mentioned formula [I], m is 0 or a positive integer, and q is 0 or 1. In addition, it is R_a when q is 1. And R_b Independently, it is a following atom or a following hydrocarbon group, and when q is 0, each joint hand joins together and 5 member rings are formed, respectively. It is R_a to R_{18} row. And R_b They are a hydrogen atom, a halogen atom, or a hydrocarbon group independently, respectively. A halogen atom is a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom here.

[0013] Moreover, as a hydrocarbon group, the alkyl group of the carbon atomic numbers 1-20, the cycloalkyl machine of the carbon atomic numbers 3-15, and an aromatic-hydrocarbon machine are independent usually mentioned, respectively. More specifically, as an alkyl group, a methyl group, an ethyl group, a propyl group, an isopropyl machine, an amyl group, a hexyl machine, an octyl machine, a decyl group, the dodecyl, and an octadecyl machine are mentioned, as a cycloalkyl machine, a cyclohexyl machine is mentioned and a phenyl group, a naphthyl group, etc. are mentioned as an aromatic-hydrocarbon machine. These hydrocarbon groups may have the halogenation machine.

[0014] The monocycle or many rings in which it could join together, respectively and a monocycle (working together mutually) or many rings could be formed in, and R_{15} - R_{18} carried out in this way, and were furthermore formed moreover in the above-mentioned formula [I] may have the double bond. The example of the monocycle formed here or many rings is shown below.

[0015] [Formula 2]

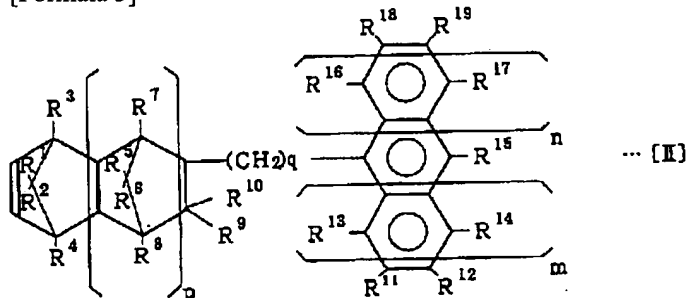


[0016] In addition, in the above-mentioned instantiation, the carbon atom with which the number of 1 or 2 was given shows the carbon atom which R_{15} (R_{16}) or R_{17} (R_{18}) have combined in a formula [I], respectively.

[0017] Moreover, it is with R_{15} and R_{16} , or the alkylidene machine may be formed by R_{17} and R_{18} . Such an alkylidene machine is usually an alkylidene machine of the carbon atomic numbers 2-20, and can mention an ethylidene machine, a propylidene machine, and an isopropylidene machine as a concrete example of such an alkylidene machine.

[0018]

[Formula 3]



[0019] q is p and 0, or a positive integer among the above-mentioned formula [II], and m and n are 0, 1, or 2. Moreover, R_1 - R_{19} are a hydrogen atom, a halogen atom, a hydrocarbon group, or an alkoxy group independently, respectively. A halogen atom is the same meaning as the halogen atom in the above-mentioned formula [I]. Moreover, as a hydrocarbon group, the alkyl group of the carbon atomic numbers 1-20, the alkyl-halide machine of the carbon atomic numbers 1-20, the cycloalkyl machine of the carbon atomic numbers 3-15, or an aromatic-hydrocarbon machine is mentioned independently, respectively. More specifically, as an alkyl group, a methyl group, an ethyl group, a propyl group, an isopropyl machine, an amyl group, a hexyl machine, an octyl machine, a decyl group, the dodecyl, and an octadecyl machine are mentioned, and it is a cycloalkyl machine. ** and a

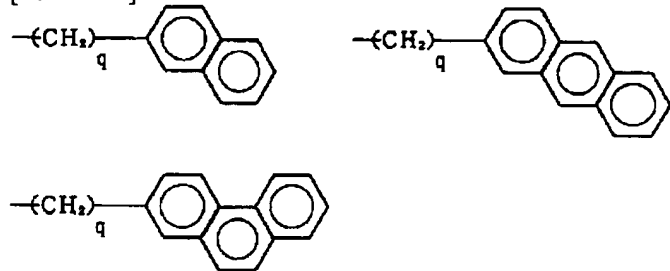
cyclohexyl machine are mentioned and a phenyl group, a tolyl group, a naphthyl group, a benzyl, a phenylethyl machine, etc. are mentioned to an aryl group and an aralkyl machine, and a concrete target as an aromatic-hydrocarbon machine. As an alkoxy group, a methoxy machine, an ethoxy basis, a propoxy group, etc. can be mentioned. The above-mentioned hydrocarbon group and the alkoxy group may have the halogenation machine.

[0020] Here, it is R9. And the carbon atom which R10 has combined, and the carbon atom which the carbon atom which R13 has combined, or R11 has combined may be combined through the alkylene machine of the direct or carbon atomic numbers 1-3. That is, it is R9 when the two above-mentioned carbon atoms have joined together through an alkylene machine. And the basis expressed with R13 or the basis expressed with R10 and R11 forms the alkylene machine of the methylene group (-CH₂-), an ethylene (-CH₂CH₂-), or the propylene machines (-CH₂CH₂CH₂-) jointly mutually.

[0021] Furthermore, at the time of n=m=0, it may join together mutually and R15, R12, or R15 and R19 may form the aromatic ring of a monocycle or many rings. The basis in which it considers as the monocycle in this case or the aromatic ring of many rings, for example, R15 and R12 form the aromatic ring further at the following times of n=m=0 is mentioned.

[0022]

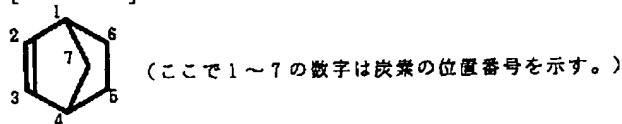
[Formula 4]



[0023] q is the same meaning as q in a formula [II] here. The annular olefin shown by above formulas [I] or [II(s)] is illustrated below more concretely.

[0024]

[Formula 5]



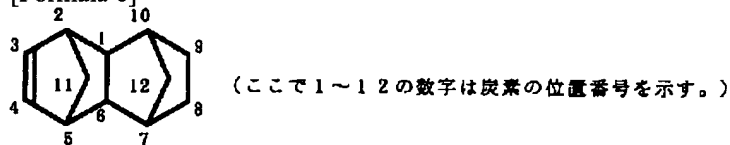
[0025] And the derivative which the hydrocarbon group replaced by this bicyclo [2.2.1]-2-heptene. As this hydrocarbon group, they are 5-methyl, 5, and 6-dimethyl, for example. 1-methyl, 5-ethyl, 5-n-butyl, 5-isobutyl, 7-methyl, 5-phenyl, a 5-methyl-5-phenyl, 5-benzyl, 5-tolyl, 5 - (ethyl phenyl) 5 5- (biphenyl), 5, - (beta-naphthyl), 5 - (alpha-naphthyl) 5 - (anthracenyl) 5 and 6-diphenyl etc. is mentioned. - (isopropyl phenyl)

[0026] As a derivative of further others, it is cyclopentadiene-acenaphthylene addition product, 1, and 4-methano. - 1, 4, 4a, 9a - A tetrahydro fluorene, 1, 4-methano - Bicyclo [2.2.1]-2-heptene derivatives, such as a 1, 4, a [4], 5, 10, and 10a-hexahydro anthracene, etc. are mentioned.

[0027] Tricyclo [4. 3.0.12, 5]-3-decene, 2-methyl tricyclo [4.3.0 . 12, 5]-3-Decene, and 5-Methyl Tricyclo [-- 4. -- Tricyclo [, Such as 3.0.12 and 5]-3-Decene, -- 4. -- 3.0.12 and 5]-3-Decene Derivative -- tricyclo [-- 4. -- 4.0.12, 5]-3-undecene, and 10-methyl tricyclo [-- 4. -- tricyclo [, such as 4.0.12 and 5]-3-undecene, -- 4. -- 4.0.12 and a 5]-3-undecene derivative

[0028]

[Formula 6]



[0029] And the derivative which the hydrocarbon group replaced by this. As this hydrocarbon group, for example 8-methyl, 8-ethyl, 8-propyl, 8-butyl and 8 - An isobutyl, 8-hexyl, 8-cyclohexyl, 8-stearyl, 5, 10-dimethyl, 2, 10-dimethyl, 8, 9-dimethyl, A 8-ethyl-9-methyl, 11, 12-dimethyl, 2 and 7, 9-TORIMECHIRU, 2, 7-dimethyl-9-ethyl, the 9-isobutyl -2, 7-dimethyl, 9, 11, 12-TORIMECHIRU, 9-ethyl -11, 12-dimethyl, The 9-isobutyl -11, 12-dimethyl, 5, 8 and 9, 10-tetramethyl, A 8-ethylidene and 8-ethylidene-9-methyl, 8-ethylidene-9-ethyl, A 8-ethylidene-9-isopropyl, 8-ethylidene-9-butyl, A 8-n-propylidene and 8-n-propylidene-9-methyl, 8-n-propylidene-9-ethyl, A 8-n-propylidene-9-isopropyl, 8-n-propylidene-9-butyl, A 8-isopropylidene and 8-isopropylidene-9-methyl, 8-isopropylidene-9-ethyl, A 8-isopropylidene-9-isopropyl, 8-isopropylidene-9-butyl, 8-chloro, 8-BUROMO, 8-fluoro, 8, 9-dichloro, 8-phenyl, a 8-methyl-8-phenyl, 8-benzyl, 8-tolyl, 8 - (ethyl phenyl) 8, - (isopropyl phenyl), 8, 9-diphenyl, 8- (biphenyl), 8, - (beta-naphthyl), 8 - (alpha-naphthyl) 8 - (anthracenyl) 5 and 6-diphenyl etc. is mentioned. As a derivative of further others, the addition product of a (cyclopentadiene-acenaphthylene addition product) and a cyclopentadiene etc. is mentioned.

[0030] PENTA cyclo [6. 5.1.13, 6.02, 7.09, 13]-4-pentadecene, and its derivative. PENTA cyclo [7. 4.0.12, 5.19, 12.08, 13]-3-pentadecene, and its derivative. PENTA cyclo [6. Pentacyclo pentadecadiene compounds, such as 5.1.13, 6.02, 7.09, 13]-4, and 10-PENTA deca diene. PENTA cyclo [8. 4.0.12, 5.19, 12.08, 13]-3-hexa decene, and its derivative. PENTA cyclo [6. 6.1.13, 6.02, 7.09, 14]-4-hexa decene, and its derivative. hexa cyclo [-- 6. -- 6.1. -- 13, 6.110, 13.02, 7.09, 14]-4-heptadecene, and its derivative heptacyclo [-- 8.7.0.12 and 9. -- 14, 7.111, and 17. -- 03, 8.012, and 16]-5- Ray KOSEN and its derivative. heptacyclo [-- 8.8.0.12 and 9. -- 14, 7.111, and 18. -- 03, 8.012, 17]-5-HENEIKOSEN, and its derivative 8.8.0.12, 9.14, 7.111 and 18.113, 16.03, octacyclo [8.012, 17]-5-DOKOSEN, and its derivative. 10.9.1.14, 7.113 and 20.115, 18.02, 10.03, and nonacyclo [8.012, 21.014, 19]-5-pen TAKOSEN and its derivative. 10.10.1.15, 8.114 and 21.116, 19.02, 11.04, and nonacyclo [9.013, 22.015, 20]-6-hexa KOSEN, its derivative, etc. are mentioned.

[0031] In addition, although the example of an annular olefin expressed with a general formula [I] or [II] was shown above, as a more concrete example of structure of these compounds, the example of structure of the annular olefin shown in paragraph number [of a specification] [0032] - [0054] at the beginning of Japanese-Patent-Application-No. 5-No. 196475 can be given.

[0032] The annular olefin expressed with above general formulas [I] or [II(s)] can be manufactured by carrying out the Diels-Alder reaction of a cyclopentadiene and the olefins which have the structure of corresponding. these annular olefins are independent -- it is -- two or more sorts can be combined and it can use

[0033] The annular olefin system resin used by this invention is choosing conditions suitably according to the method which these people proposed in official reports, such as JP,60-168708,A, 61-120816, 61-115912, 61-115916, 61-271308, 61-272216, 62-252406, and 62-252407, using the annular olefin expressed with above formulas [I] or [II(s)]. It can manufacture.

[0034] as the annular olefin system resin obtained from the above annular olefins in an annular olefin system resin this invention -- concrete -- (i) The random copolymer of ethylene and an annular olefin, the ring-opening-polymerization object of (ii) annular olefin, or copolymer (iii), The hydride of a ring-opening-polymerization object or a copolymer, and (iv) above (i) (ii) -- or (iii) A graft denaturation object is mentioned.

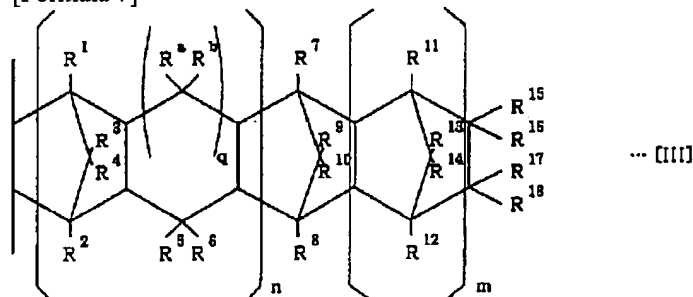
[0035] (i) the unit to which ethylene and an annular olefin random copolymer are led from ethylene -- usually -- 52-90-mol % -- the unit which is % of the amount of 55-80 mols preferably, and is drawn from an annular olefin -- usually -- 10-48-mol % -- it is desirable to contain in % of the amount of 20-45 mols preferably In addition, the ethylene unit content and annular olefin unit content of a copolymer can be measured by ¹³C-NMR.

[0036] this ethylene and annular olefin random copolymer (i) **** -- the unit drawn from the above ethylene, and the unit drawn from an annular olefin -- random -- arranging -- joining together -- substantial -- a line -- it has structure This copolymer is a line substantially, and when this copolymer is dissolved in an organic solvent, it can check not having the gel structure of cross linkage substantially by not containing insoluble matter in this solution. For example, it can check by dissolving in a 135-degree C decalin completely.

[0037] It is thought that a part of annular olefin [at least] shown by the above-mentioned formula [I] or [II] constitutes the repeat unit shown by the following formula [III] or [IV] from ethylene and an annular olefin random copolymer.

[0038]

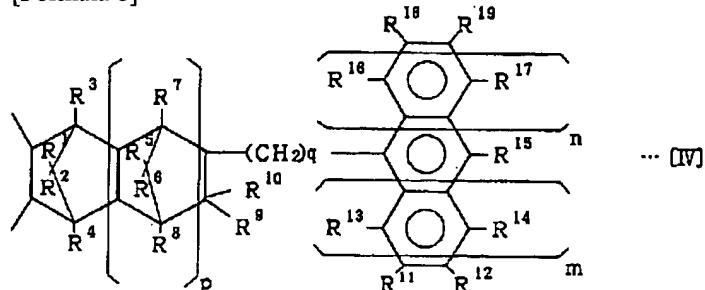
[Formula 7]



[0039] (In a formula [III], Ra and Rb are the same meanings as the same sign in a formula [I] at n, m, q, R1 - R18 row.)

[0040]

[Formula 8]



[0041] (In a formula [IV], n, m, p, q, and R1-R19 are the same meanings as the same sign in a formula [II].)

Moreover, the above ethylene and annular olefin random copolymers may have the unit drawn from the monomer in which other

copolymerization is possible if needed in the range which does not spoil the purpose of this invention.

[0042] As such other monomers Olefins other than **, the above ethylene, or an annular olefin can be mentioned. specifically A propylene, 1-butene, 1-pentene, 1-hexene, a 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4, and 4-dimethyl-1-hexene, 4, and 4-dimethyl-1-pentene, A 4-ethyl-1-hexene, a 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecen, 1-tetrapod decene, 1-hexa decene, The alpha olefin of the carbon numbers 3-20, such as 1-octadecene and 1-ray KOSEN A cyclobutene, a cyclopentene, a cyclohexene, 3, 4-dimethyl cyclopentene, 3-methyl cyclohexene, a 2-(2-methyl butyl)-1-cyclohexene, and a cyclo octene, 3a, 5, 6, 7a-tetrahydro - Cycloolefins, such as a 4 and 7-methano-1H-indene, 2-norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-isopropyl-2-norbornene, 5-n-butyl-2-norbornene, 5-isobutyl-2-norbornene, 5, 6-dimethyl-2-norbornene, Norbornene, such as 5-chloro-2-norbornene and 5-fluoro-2-norbornene 1, 4-hexadiene, the 4-methyl -1, 4-hexadiene, the 5-methyl -1, 4-hexadiene, Nonconjugated diene, such as 1, 7-OKUTA diene, a dicyclopentadiene, 5-ethylidene-2-norbornene, and 5-vinyl-2-norbornene, can be mentioned.

[0043] Ethylene and annular olefin random copolymer (i) You may usually contain less than [20 mol %] and two or more sorts of units which may contain in the amount not more than 10 mol % preferably, and are drawn from other monomers for the unit drawn from other above monomers.

[0044] The above ethylene and annular olefin random copolymers (i) It can manufacture by the manufacture method indicated by the above-mentioned official report using the annular olefin shown by ethylene, the formula [I], or [II]. It is desirable to manufacture ethylene and an annular olefin random copolymer using the catalyst which performs this copolymerization in a hydrocarbon solvent and is formed in this hydrocarbon solvent from the vanadium compound and organoaluminium compound of fusibility as a catalyst also among these.

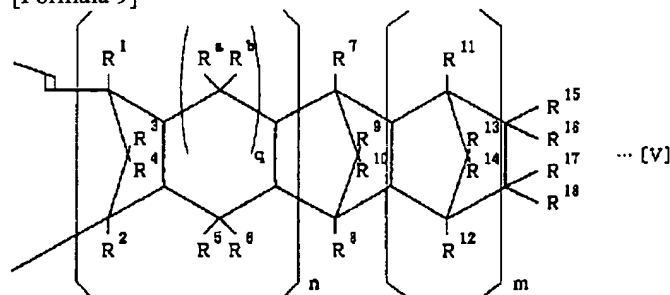
[0045] Moreover, at this copolymerization reaction, a solid-state-like IVB group metallocene system catalyst can also be used. A solid-state-like IVB group metallocene system catalyst is a catalyst which consists of the transition-metals compound containing the ligand which has a cyclopentadienyl skeleton, an organic aluminum oxy compound, and an organoaluminium compound blended by the need here. As an IVB group's transition metals, it is a zirconium, titanium, or a hafnium and these transition metals have the ligand containing at least one cyclopentadienyl skeleton here. Here, the cyclopentadienyl group which the alkyl group may replace as an example of the ligand containing a cyclopentadienyl skeleton or an indenyl group, a tetrahydro indenyl group, and a FUROORENIRU machine can be mentioned. These bases may be combined through other bases, such as an alkylene machine. Moreover, ligands other than the ligand containing a cyclopentadienyl skeleton are an alkyl group, a cycloalkyl machine, an aryl group, an aralkyl machine, etc.

[0046] Furthermore, what is usually used for manufacture of an olefin system resin can be used for an organic aluminum oxy compound and an organoaluminium compound. Such a solid-state-like IVB group metallocene system catalyst is indicated by JP,61-221206,A, 64-106, JP,1-173112,A, etc.

[0047] It is thought that a part of annular olefin [at least] shown by the above-mentioned formula [I] or [II] constitutes the repeat unit shown by the following formula [V] or [VI] from the ring-opening-polymerization object or ring breakage copolymer of (ii) annular olefin used by this invention.

[0048]

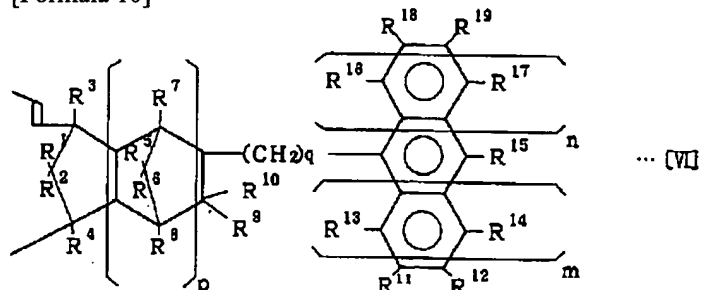
[Formula 9]



[0049] (In a formula [III], Ra and Rb are the same meanings as the same sign in a formula [I] at n, m, q, R1 - R18 row.)

[0050]

[Formula 10]



[0051] (In a formula [IV], n, m, p, q, and R1 - R19 are the same meanings as the same sign in a formula [II].)

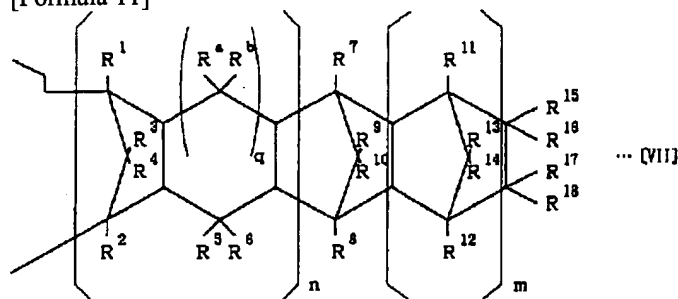
The annular olefin which can manufacture the above ring breakage (**) polymers (ii) by the manufacture method indicated by the aforementioned official report, for example, is expressed with the above-mentioned formula [I] can be manufactured a polymerization or by carrying out copolymerization under existence of a ring-opening-polymerization catalyst.

[0052] The catalyst which consists of the metaled halogenide or acetylaceton compound chosen from the catalyst which consists of the halogenide of the metal chosen from a ruthenium, a rhodium, palladium, an osmium, an indium, or platinum, a nitrate or an acetylaceton compound, and a reducing agent as a ring-opening-polymerization catalyst or titanium, palladium, a zirconium, or molybdenum, and an organoaluminium compound can be used.

[0053] (iii) The hydride of a ring breakage (**) polymer hydrogenates above ring-opening-polymerization objects or ring breakage copolymers (ii) under existence of well-known catalysts for hydrogenation conventionally, and is obtained. hydride (iii) of this ring breakage (**) polymer **** -- it is thought that a part of unit [at least] drawn from a formula [I] or [II] is expressed with the following formula [VII] or [VIII]

[0054]

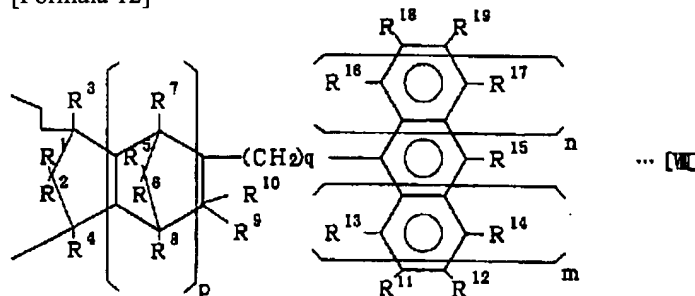
[Formula 11]



[0055] (In a formula [VII], Ra and Rb are the same meanings as the same sign in a formula [I] at n, m, q and R1 - R18 row.)

[0056]

[Formula 12]



[0057] (In a formula [VIII], n, m, p, q, and R1 -R19 are the same meanings as the same sign in a formula [II].)

(iv) -- the ethylene and annular olefin random copolymer of the above [the graft denaturation object of an annular olefin system resin] (i) Graft denaturation object (iii) of the hydride of the ring-opening-polymerization object of an annular olefin, a copolymer (ii), or a ring breakage (**) polymer it is .

[0058] As this modifier ** -- usually -- an unsaturation carvone -- acids use -- having -- concrete (meta) -- acrylic-acid, maleic-acid, fumaric-acid, tetrahydrophthal acid, itaconic-acid, citraconic-acid, crotonic-acid, isocrotonic-acid, and endo-cis-bicyclo -- [2.2.1] Hept-5- unsaturated carboxylic acids, such as an en -2 and 3-dicarboxylic acid (NAJIKKU acid TM), -- the derivative of these unsaturated carboxylic acids, for example, an unsaturation carvone acid anhydride, unsaturated-carboxylic-acid halide, an unsaturation carvone acid amide, an unsaturation carvone acid imide, the ester compound of a unsaturated carboxylic acid, etc. are As a derivative of a unsaturated carboxylic acid, maleic-anhydride, anhydrous citraconic-acid, and chlorination MARENIRU, maleimide, maleic-acid monomethyl, a maleic-acid dimethyl, glycidil maleate, etc. are mentioned more concretely.

[0059] these modifiers -- the anhydride of alpha and beta-unsaturation dicarboxylic-acid and alpha, and beta-unsaturation dicarboxylic-acid anhydride, for example, a maleic acid, a NAJIKKU acid, and these acids is used preferably also in inside Two or more sorts of these modifiers can be combined, and they can also be used.

[0060] As for the rate of denaturation in the graft denaturation object of the annular olefin system resin used by this invention, it is desirable that it is usually less than [10 mol %]. Such a graft denaturation object of an annular olefin system resin can blend and carry out the graft polymerization of the modifier to an annular olefin system resin, can also be manufactured so that it may become a desired rate of denaturation, can prepare the denaturation object of the rate of high denaturation beforehand, and can also manufacture it by subsequently mixing this denaturation object and the annular olefin system resin of native.

[0061] In order to obtain the graft denaturation object of an annular olefin system resin from an annular olefin system resin and a modifier, the denaturation method of well-known polymer is widely applicable conventionally. For example, a graft denaturation object can be obtained by the method of adding and carrying out the graft polymerization (reaction) of the modifier to the annular olefin system resin in a melting state, or the method of adding a modifier in the solvent solution of an annular olefin

system resin, and carrying out a graft reaction.

[0062] Such a graft reaction is usually performed at the temperature of 60-350 degrees C. Moreover, a graft reaction can be performed to the bottom of coexistence of radical initiators, such as organic peroxide and an azo compound.

[0063] Moreover, the above denaturation objects of the rate of denaturation can also be obtained by diluting so that it may become the rate of denaturation of a request of this denaturation object with the annular olefin system resin of native, after being able to obtain directly by the graft reaction of an annular olefin system resin and a modifier and obtaining the denaturation object of the rate of high denaturation beforehand by the graft reaction of an annular olefin system resin and a modifier.

[0064] The (i) above as an annular olefin system resin in this invention Either (ii) and (iii) (iv) may be used, and you may use combining these. Also among these, they are ethylene and an annular olefin random copolymer (i). It is used especially preferably.

[0065] In this invention, the annular olefin system resin Plastic solid processed by steam or hot water is obtained by fabricating the above annular olefin system resins by methods, such as an injection-blow-molding method, well-known forming method, for example, injection-molding method, a direct-blow-molding method, a T die method, a tubular film process, and the pressing method.

[0066] The configuration of a Plastic solid is not limited especially that what is necessary is just a request configuration according to the purposes of use, such as the shape of the shape of the shape of a container, and a tray, the shape of a sheet, and a film. As long as this annular olefin system resin Plastic solid is a range which does not spoil the purpose of this invention, it may contain other components arbitrarily. As other components, stabilizers, such as a heat-resistant stabilizer and a weathering stabilizer, a cross linking agent, a bridge formation assistant, an antistatic agent, a slipping agent, an anti blocking agent, an antifogger, lubricant, a color, a pigment, a straight-mineral-oil system softener, a petroleum resin, a wax, etc. can also be used.

[0067] As the stabilizer contained as this arbitrary component For example, fatty-acid metal salts, such as a phenol system antioxidant [, such as tetrakis [methylene-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate] methane, beta-(3, 5-G t-butyl-4-hydroxyphenyl) propionic-acid alkyl ester, 2, and 2'-OGIZAMIDOBISU [ethyl-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate,], zinc-stearate, calcium-stearate, 1, and 2-hydroxy calcium stearate, These can also be combined and used, for example, can also be used combining tetrakis [methylene-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate] methane, a zinc stearate, or a calcium stearate.

[0068] Moreover, it is a stabilizer. For example, distearyl pentaerythritol diphosphite, II (nonylphenyl) pentaerythritol diphosphite, A phenyl -4, 4'-isopropylidene diphenol-pentaerythritol diphosphite, Bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, Screw (2, 6-G t-butyl-4-methylphenyl) pentaerythritol diphosphite, Phenyl bisphenol-A-pentaerythritol diphosphite, A tris (2, 4-G t-buthylphenyl) force fight, a tris (nonylphenyl) force fight, The Lynn system stabilizers, such as tetrakis (2, 4-G t-buthylphenyl) -4, 4'-biphenylene diphosphite, and screw (2, 6-G t-butyl-4-methylphenyl) pentaerythritol diphosphite, are mentioned.

[0069] Moreover, the fatty acid ester of polyhydric alcohol can be used as other components. As this polyhydric alcohol, the polyhydric alcohol more than trivalent, for example, a glycerol, a pentaerythritol, etc. are mentioned. Moreover, as a fatty acid, the aliphatic monocarboxylic acid of carbon numbers 5-20 is mentioned, for example, a lauric acid, a myristic acid, a palmitic acid, stearin acid, etc. are mentioned. Among these, the partial ester of polyhydric alcohol is then used preferably. The fatty acid ester of pentaerythritols, such as glycerine fatty acid esters, such as glycerine monolaurate, a glycerol monochrome millimeter state, glycerol monopalmitate, glycerol monostearate, glycerol dilaurate, and glycerol distearate, pentaerythritol monochrome laurate, pentaerythritol monostearate, pentaerythritol dilaurate, pentaerythritol distearate, and pentaerythritol tristearate, is used preferably concretely.

[0070] Moreover, an annular olefin system resin is even if it is the range which does not spoil the purpose of this invention and contains the organic filler or the inorganic filler. It may be good, for example, a silica, diatomaceous earth, an alumina, titanium oxide, a magnesium oxide, a pumice powder, a pumice balloon, an aluminum hydroxide, a magnesium hydroxide, a basic magnesium carbonate, a dolomite, a calcium sulfate, a potassium titanate, a barium sulfate, a calcium sulfite, talc, clay, a mica, asbestos, glass flakes, a glass bead, a calcium silicate, a montmorillonite, a bentonite, graphite, the aluminium powder, the molybdenum sulfide, etc. may be contained. The annular olefin system resin Plastic solid may contain two or more sorts of other components.

[0071] In steam processing of a Plastic solid, or a hot water art this invention, above hot water processings or steam processings of an annular olefin system resin Plastic solid are performed as follows. Hot water processing or steam processing of a Plastic solid is performed by being carried out under the sterilization processing conditions by the sterilization using usual hot water or usual steam, for example, contacting the hot shape of a gas and hot liquefied water to this Plastic solid by methods, such as sterilization by high pressure steam, such as the autoclave method and the steam method, and boiling method. The steam at the time of sterilization processing or the temperature (T degrees C) of hot water is usually 80 degrees C or more, and the processing time is usually more than for 5 minutes.

[0072] the time (T-50) of making processing temperature by hot water or steam into T degrees C in this invention immediately after processing by above-mentioned hot water or above-mentioned steam -- temperature higher than ** -- more than ** (T-30), it is the temperature more than ** (T-20) still more preferably, and holds more than for 20 minutes preferably more than for 10 minutes in 20% or less of atmosphere preferably [50% or less of relative humidity] In addition, the upper limit of this retention temperature should just be temperature which does not spoil the configuration of a Plastic solid. Thus, in case it moves in the hot blast oven held at the above-mentioned atmosphere and holds after carrying out the steam sterilization of the Plastic solid for example, within an autoclave, it is desirable to move the Plastic solid after steam processing in oven promptly.

[0073] Thus, by holding in the above-mentioned atmosphere immediately after hot water processing or steam processing, the milkiness (cloudiness) by hot water processing or steam processing of an annular olefin system resin Plastic solid can be prevented.

[0074] According to such this invention, even if it performs sterilization processing to an annular olefin system resin Plastic solid, the transparency of this Plastic solid and appearance are not spoiled. Moreover, in this invention, since a white blush mark can be prevented as mentioned above even if an annular olefin system resin Plastic solid has not contained the additive for milkiness prevention, it is suitably used as medical devices, such as medical-supplies containers, such as medicine tools, for example, the Bayh Al bottle, by which especially steam sterilization is carried out, a tablet bottle, a prefilled syringe, a test tube, and a petri dish, a diamond riser, and a waste blood tank, or a food container by which hot water processing is carried out.

[0075]

[Effect of the Invention] According to the steam or the hot water art of the above annular olefin system resin Plastic solids, sterilization processing of the annular olefin system resin Plastic solid can be carried out by steam or hot water, without producing a white blush mark.

[0076]

[Example] Next, although an example explains this invention concretely, this invention is not limited to these examples. In addition, it set to this invention, and the following method measured or estimated various physical properties.

[0077] (1) Softening temperature temperature (TMA)

Du Pont make It measured by the heat deformation behavior of a sheet with a thickness of 1mm using Thermal Mechanical Analyzer. The needle made from a quartz was put on the sheet, 49g of loads was applied, the temperature up was carried out the speed for 5-degree-C/, and temperature at which the needle invaded 0.635mm into the sheet was set to TMA.

(2) Glass transition temperature (Tg)

the product made from SEIKO Electronic industry -- it measured by part for 10 degrees-C/of programming rates using DSC-20

(3) a light transmission and Hayes -- respectively -- ASTM It measured based on D1003.

[0078]

[Example 1] Softening temperature temperature (TMA) was 155 degrees C (Tg=144 degree C), and MFR (260 degrees C, measurement under a condition which is 2160g) carried out injection molding of the ethylene norbornene copolymer for 10g / 10 minutes, and obtained the corner guard with a thickness of 2mm. Hayes of this corner guard is shown in Table 1.

[0079] The steam processing above-mentioned corner guard was put into the autoclave, and steam processing was carried out for 20 minutes at 121 degrees C. After the steam processing end, the corner guard was immediately taken out from the autoclave and it heated in the atmosphere of 5% of relative humidity in the hot blast oven set as 120 degrees C for 2 hours. Hayes of the corner guard after the above-mentioned processing is shown in Table 1.

[0080]

[The example 1 of comparison] The corner guard obtained by carrying out injection molding like an example 1 was left for 2 hours in 23 degrees C and the interior of a room of 50% of relative humidity, after carrying out steam processing for 20 minutes at 121 degrees C. Hayes of the corner guard after processing is shown in Table 1.

[0081]

[Table 1]

		実施例 1	比較例 1
ヘイズ (%)	スチーム処理前	1. 2	
	スチーム処理後	1. 2	3. 3

[Translation done.]

*** NOTICES ***

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- 2.**** shows the word which can not be translated.
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TECHNICAL FIELD

[Field of the Invention] this invention relates to the steam or the hot water art of an annular olefin system resin Plastic solid which can carry out sterilization processing by steam or hot water, without making an annular olefin system resin Plastic solid milk.

[0002]

Background of the Invention] A polyolefine is non-toxicity, and is excellent in transparency, has properties, such as a thermoforming plain-gauze cone, and is used for the use more extensive than before. if compared with alpha olefins, such as ethylene and a propylene, also among such polyolefines -- ** -- the annular olefin system resin obtained from the annular olefin which has high structure is excellent in transparency, thermal resistance, rigidity, dampproofing, etc. compared with polyethylene, polypropylene, etc., and use for various uses is studied

[0003] Especially this annular olefin system resin also has the property that the sterilization processing by steam or hot water is possible, and is suitable as molding materials, such as medical treatment and medicine tools which perform such sterilization processing, or a food-grade container.

[0004] However, the Plastic solid which consists of this annular olefin system resin has the trouble that milkiness (cloudiness) may be produced in a Plastic solid and transparency may fall to it, when steam or hot water performs sterilization processing.

[0005] Although how to include the additive for preventing a white blush mark for example, in an annular olefin system resin Plastic solid as the solution method of such a trouble etc. can be considered, as for especially the Plastic solid used for medical treatment and a medicine use, it is desirable not to include an additive etc. as much as possible.

[0006] For this reason, an art by the steam or hot water of an annular olefin system resin Plastic solid which can perform sterilization processing by steam or hot water was desired, without producing a white blush mark, even if it did not include the additive for milkiness prevention etc. in an annular olefin system resin Plastic solid.

[0007]

[Objects of the Invention] this invention is made in view of the above conventional technology, and it aims at offering the steam or the hot water art of an annular olefin system resin Plastic solid which can carry out sterilization processing by steam or hot water, without making an annular olefin system resin Plastic solid milk.

[0008]

[Summary of the Invention] When the steam or the hot water art of an annular olefin system resin Plastic solid concerning this invention makes this processing temperature T degrees C immediately after steam-processing or hot water processing the Plastic solid which the softening temperature temperature measured with a thermal mechanical analyzer becomes from the annular olefin system resin which is 110 degrees C or more (T-50) It is temperature higher than **, and is characterized by holding 10 minutes or more in the atmosphere of 50% or less of relative humidity. As for the above-mentioned annular olefin system resin, it is desirable that it is the random copolymer of ethylene and an annular olefin.

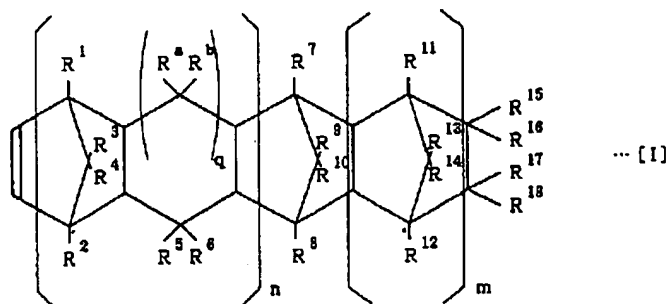
[0009]

[Detailed Description of the Invention] The steam or the hot water art of an annular olefin system resin Plastic solid which starts this invention below is explained concretely. In the steam or the hot water art of an annular olefin system resin Plastic solid concerning this invention, the Plastic solid which consists of an annular olefin system resin is steam-processed or hot water processed by method which is mentioned later.

[0010] Although the annular olefin system resin whose softening temperature temperature measured with a thermal mechanical analyzer is 110 degrees C or more is used in this invention, this annular olefin system resin is obtained from the annular olefin shown by the following formula [I] or [II]. This annular olefin is explained first.

[0011]

[Formula 1]



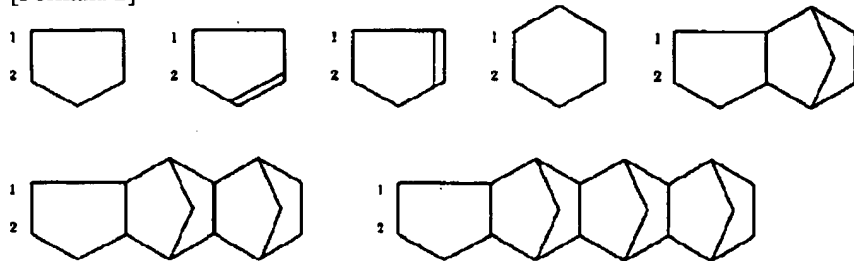
[0012] n is 0 or 1 among the above-mentioned formula [I], m is 0 or a positive integer, and q is 0 or 1. In addition, it is R_a when q is 1. And R_b Independently, it is a following atom or a following hydrocarbon group, and when q is 0, each joint hand joins together and 5 member rings are formed, respectively. It is R_a to R_{18} row. And R_b They are a hydrogen atom, a halogen atom, or a hydrocarbon group independently, respectively. A halogen atom is a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom here.

[0013] Moreover, as a hydrocarbon group, the alkyl group of the carbon atomic numbers 1-20, the cycloalkyl machine of the carbon atomic numbers 3-15, and an aromatic-hydrocarbon machine are independent usually mentioned, respectively. More specifically, as an alkyl group, a methyl group, an ethyl group, a propyl group, an isopropyl machine, an amyl group, a hexyl machine, an octyl machine, a decyl group, a dodecyl machine, and an octadecyl machine are mentioned, as a cycloalkyl machine, a cyclohexyl machine is mentioned and a phenyl group, a naphthyl group, etc. are mentioned as an aromatic-hydrocarbon machine. These hydrocarbon groups may have the halogenation machine.

[0014] The monocycle or many rings in which it could join together, respectively and a monocycle (working together mutually) or many rings could be formed in, and R_{15} - R_{18} carried out in this way, and were furthermore formed moreover in the above-mentioned formula [I] may have the double bond. The example of the monocycle formed here or many rings is shown below.

[0015]

[Formula 2]

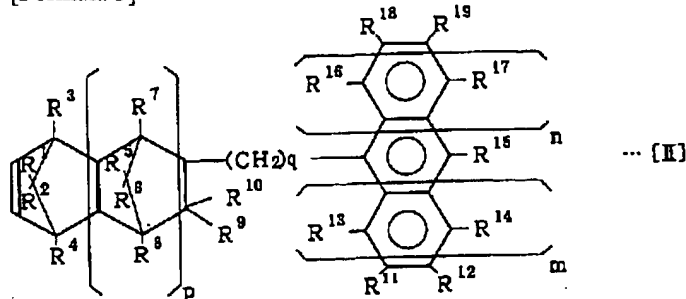


[0016] In addition, in the above-mentioned instantiation, the carbon atom with which the number of 1 or 2 was given shows the carbon atom which R_{15} (R_{16}) or R_{17} (R_{18}) have combined in a formula [I], respectively.

[0017] Moreover, it is with R_{15} and R_{16} , or the alkylidene machine may be formed by R_{17} and R_{18} . Such an alkylidene machine is usually an alkylidene machine of the carbon atomic numbers 2-20, and can mention an ethylidene machine, a propylidene machine, and an isopropylidene machine as a concrete example of such an alkylidene machine.

[0018]

[Formula 3]



[0019] q is p and 0, or a positive integer among the above-mentioned formula [II], and m and n are 0, 1, or 2. Moreover, R_1 - R_{19} are a hydrogen atom, a halogen atom, a hydrocarbon group, or an alkoxy group independently, respectively. A halogen atom is the same meaning as the halogen atom in the above-mentioned formula [I]. Moreover, as a hydrocarbon group, the alkyl group of the carbon atomic numbers 1-20, the alkyl-halide machine of the carbon atomic numbers 1-20, the cycloalkyl machine of the carbon atomic numbers 3-15, or an aromatic-hydrocarbon machine is mentioned independently, respectively. More specifically, as an alkyl group, a methyl group, an ethyl group, a propyl group, an isopropyl machine, an amyl group, a hexyl machine, an

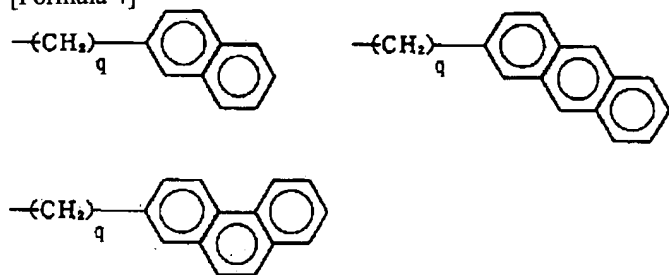
octyl machine, a decyl group, a dodecyl machine, and an octadecyl machine are mentioned, and it is a cycloalkyl machine. ** and a cyclohexyl machine are mentioned and a phenyl group, a tolyl group, a naphthyl group, a benzyl, a phenylethyl machine, etc. are mentioned to an aryl group and an aralkyl machine, and a concrete target as an aromatic-hydrocarbon machine. As an alkoxy group, a methoxy machine, an ethoxy basis, a propoxy group, etc. can be mentioned. The above-mentioned hydrocarbon group and the alkoxy group may have the halogenation machine.

[0020] Here, it is R9. And the carbon atom which R10 has combined, and the carbon atom which the carbon atom which R13 has combined, or R11 has combined may be combined through the alkylene machine of the direct or carbon atomic numbers 1-3. That is, it is R9 when the two above-mentioned carbon atoms have joined together through an alkylene machine. And the basis expressed with R13 or the basis expressed with R10 and R11 forms the alkylene machine of the methylene group (-CH₂-), an ethylene (-CH₂CH₂-), or the propylene machines (-CH₂CH₂CH₂-) jointly mutually.

[0021] Furthermore, at the time of n=m=0, it may join together mutually and R15, R12, or R15 and R19 may form the aromatic ring of a monocycle or many rings. The basis in which it considers as the monocycle in this case or the aromatic ring of many rings, for example, R15 and R12 form the aromatic ring further at the following times of n=m=0 is mentioned.

[0022]

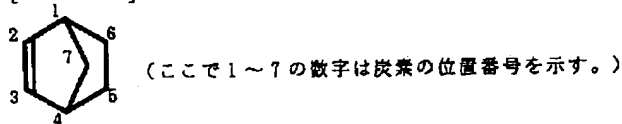
[Formula 4]



[0023] q is the same meaning as q in a formula [II] here. The annular olefin shown by above formulas [I] or [II(s)] is illustrated below more concretely.

[0024]

[Formula 5]



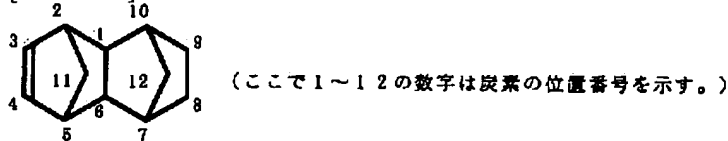
[0025] And the derivative which the hydrocarbon group replaced by this bicyclo [2.2.1]-2-heptene. As this hydrocarbon group, they are 5-methyl, 5, and 6-dimethyl, for example. 1-methyl, 5-ethyl, 5-n-butyl, 5-isobutyl, 7-methyl, 5-phenyl, a 5-methyl-5-phenyl, 5-benzyl, 5-tolyl, 5 - (ethyl phenyl) 5 5- (biphenyl), 5, - (beta-naphthyl), 5 - (alpha-naphthyl) 5 - (anthracenyl) 5 and 6-diphenyl etc. is mentioned. - (isopropyl phenyl)

[0026] As a derivative of further others, it is cyclopentadiene-acenaphthylene addition product, 1, and 4-methano. - 1, 4, 4a, 9a - A tetrahydro fluorene, 1, 4-methano - Bicyclo [2.2.1]-2-heptene derivatives, such as a 1, 4, a [4], 5, 10, and 10a-hexahydro anthracene, etc. are mentioned.

[0027] Tricyclo [4. 3.0.12, 5]-3-decene, 2-methyl tricyclo [4.3.0 . 12, 5]-3-Decene, and 5-Methyl Tricyclo [-- 4. -- Tricyclo [, Such as 3.0.12 and 5]-3-Decene, -- 4. -- 3.0.12 and 5]-3-Decene Derivative -- tricyclo [-- 4. -- 4.0.12, 5]-3-undecene, and 10-methyl tricyclo [-- 4. -- tricyclo [, such as 4.0.12 and 5]-3-undecene, -- 4. -- 4.0.12 and a 5]-3-undecene derivative

[0028]

[Formula 6]



[0029] And the derivative which the hydrocarbon group replaced by this. As this hydrocarbon group, for example 8-methyl, 8-ethyl, 8-propyl, 8-butyl and 8 - An isobutyl, 8-hexyl, 8-cyclohexyl, 8-stearyl, 5, 10-dimethyl, 2, 10-dimethyl, 8, 9-dimethyl, A 8-ethyl-9-methyl, 11, 12-dimethyl, 2 and 7, 9-TORIMECHIRU, 2, 7-dimethyl-9-ethyl, the 9-isobutyl -2, 7-dimethyl, 9, 11, 12-TORIMECHIRU, 9-ethyl -11, 12-dimethyl, The 9-isobutyl -11, 12-dimethyl, 5, 8 and 9, 10-tetramethyl, A 8-ethylidene and 8-ethylidene-9-methyl, 8-ethylidene-9-ethyl, A 8-ethylidene-9-isopropyl, 8-ethylidene-9-butyl, A 8-n-propylidene and 8-n-propylidene-9-methyl, 8-n-propylidene-9-ethyl, A 8-n-propylidene-9-isopropyl, 8-n-propylidene-9-butyl, A 8-isopropylidene and 8-isopropylidene-9-methyl, 8-isopropylidene-9-ethyl, A 8-isopropylidene-9-isopropyl, 8-isopropylidene-9-butyl, 8-chloro, 8-BUROMO, 8-fluoro, 8, 9-dichloro, 8-phenyl, a 8-methyl-8-phenyl, 8-benzyl, 8-tolyl, 8 - (ethyl phenyl) 8, - (isopropyl phenyl), 8, 9-diphenyl, 8- (biphenyl), 8, - (beta-naphthyl), 8 - (alpha-naphthyl) 8 - (anthracenyl) 5 and 6-diphenyl etc. is mentioned. As a derivative of further others, the addition product of a (cyclopentadiene-acenaphthylene addition product) and a cyclopentadiene

etc. is mentioned.

[0030] PENTA cyclo [6. 5.1.13, 6.02, 7.09, 13]-4-pentadecene, and its derivative. PENTA cyclo [7. 4.0.12, 5.19, 12.08, 13]-3-pentadecene, and its derivative. PENTA cyclo [6. Pentacyclo pentadecadiene compounds, such as 5.1.13, 6.02, 7.09, 13]-4, and 10-PENTA deca diene. PENTA cyclo [8. 4.0.12, 5.19, 12.08, 13]-3-hexa decene, and its derivative. PENTA cyclo [6. 6.1.13, 6.02, 7.09, 14]-4-hexa decene, and its derivative. hexa cyclo [-- 6. -- 6.1. -- 13, 6.110, 13.02, 7.09, 14]-4-heptadecene, and its derivative heptacyclo [-- 8.7.0.12 and 9. -- 14, 7.111, and 17. -- 03, 8.012, and 16]-5- Ray KOSEN and its derivative. heptacyclo [-- 8.8.0.12 and 9. -- 14, 7.111, and 18. -- 03, 8.012, 17]-5-HENEIKOSEN, and its derivative 8.8.0.12, 9.14, 7.111 and 18.113, 16.03, octacyclo [8.012, 17]-5-DOKOSEN, and its derivative. 10.9.1.14, 7.113 and 20.115, 18.02, 10.03, and nonacyclo [8.012, 21.014, 19]-5-pen TAKOSEN and its derivative. 10.10.1.15, 8.114 and 21.116, 19.02, 11.04, and nonacyclo [9.013, 22.015, 20]-6-hexa KOSEN, its derivative, etc. are mentioned.

[0031] In addition, although the example of an annular olefin expressed with a general formula [I] or [II] was shown above, as a more concrete example of structure of these compounds, the example of structure of the annular olefin shown in paragraph number [of a specification] [0032] - [0054] at the beginning of Japanese-Patent-Application-No. 5-No. 196475 can be given.

[0032] The annular olefin expressed with above general formulas [I] or [II(s)] can be manufactured by carrying out the Diels-Alder reaction of a cyclopentadiene and the olefins which have the structure of corresponding. these annular olefins are independent -- it is -- two or more sorts can be combined and it can use

[0033] The annular olefin system resin used by this invention is choosing conditions suitably according to the method which these people proposed in official reports, such as JP,60-168708,A, 61-120816, 61-115912, 61-115916, 61-271308, 61-272216, 62-252406, and 62-252407, using the annular olefin expressed with above formulas [I] or [II(s)]. It can manufacture.

[0034] as the annular olefin system resin obtained from the above annular olefins in an annular olefin system resin this invention -- concrete -- (i) The random copolymer of ethylene and an annular olefin, the ring-opening-polymerization object of (ii) annular olefin, or copolymer (iii), The hydride of a ring-opening-polymerization object or a copolymer, and (iv) above (i) (ii) -- or (iii) A graft denaturation object is mentioned.

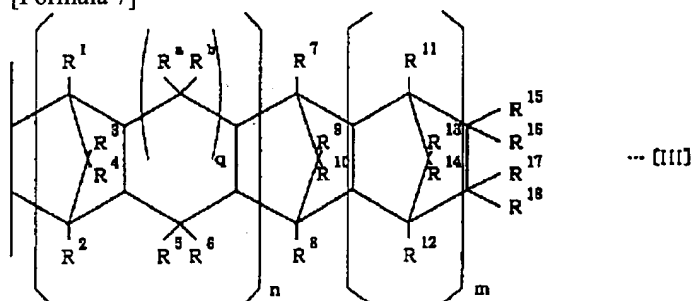
[0035] (i) the unit to which ethylene and an annular olefin random copolymer are led from ethylene -- usually -- 52-90-mol % -- the unit which is % of the amount of 55-80 mols preferably, and is drawn from an annular olefin -- usually -- 10-48-mol % -- it is desirable to contain in % of the amount of 20-45 mols preferably In addition, the ethylene unit content and annular olefin unit content of a copolymer can be measured by ^{13}C -NMR.

[0036] this ethylene and annular olefin random copolymer (i) **** -- the unit drawn from the above ethylene, and the unit drawn from an annular olefin -- random -- arranging -- joining together -- substantial -- a line -- it has structure This copolymer is a line substantially, and when this copolymer is dissolved in an organic solvent, it can check not having the gel structure of cross linkage substantially by not containing insoluble matter in this solution. For example, it can check by dissolving in a 135-degree C decalin completely.

[0037] It is thought that a part of annular olefin [at least] shown by the above-mentioned formula [I] or [II] constitutes the repeat unit shown by the following formula [III] or [IV] from ethylene and an annular olefin random copolymer.

[0038]

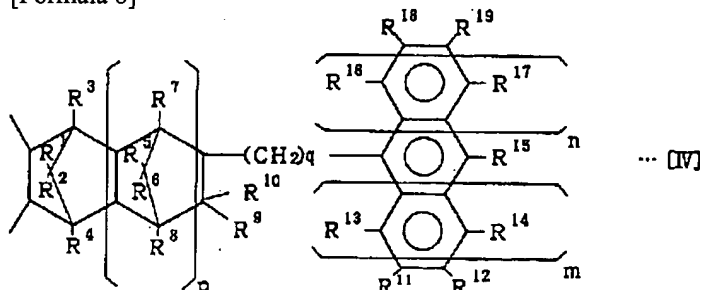
[Formula 7]



[0039] (In a formula [III], Ra and Rb are the same meanings as the same sign in a formula [I] at n, m, q, R1 - R18 row.)

[0040]

[Formula 8]



[0041] (In a formula [IV], n, m, p, q, and R1-R19 are the same meanings as the same sign in a formula [II].)

Moreover, the above ethylene and annular olefin random copolymers may have the unit drawn from the monomer in which other copolymerization is possible if needed in the range which does not spoil the purpose of this invention.

[0042] As such other monomers Olefins other than **, the above ethylene, or an annular olefin can be mentioned. specifically A propylene, 1-butene, 1-pentene, 1-hexene, a 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4, and 4-dimethyl-1-hexene, 4, and 4-dimethyl-1-pentene, A 4-ethyl-1-hexene, a 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecen, 1-tetrapod decene, 1-hexa decene, The alpha olefin of the carbon numbers 3-20, such as 1-octadecene and 1-ray KOSSEN A cyclobutene, a cyclopentene, a cyclohexene, 3, 4-dimethyl cyclopentene, 3-methyl cyclohexene, a 2-(2-methyl butyl)-1-cyclohexene, and a cyclo octene, 3a, 5, 6, 7a-tetrahydro - Cycloolefins, such as a 4 and 7-methano-1H-indene, 2-norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-isopropyl-2-norbornene, 5-n-butyl-2-norbornene, 5-isobutyl-2-norbornene, 5, 6-dimethyl-2-norbornene, Norbornene, such as 5-chloro-2-norbornene and 5-fluoro-2-norbornene 1, 4-hexadiene, the 4-methyl -1, 4-hexadiene, the 5-methyl -1, 4-hexadiene, Nonconjugated diene, such as 1, 7-OKUTA diene, a dicyclopentadiene, 5-ethylidene-2-norbornene, and 5-vinyl-2-norbornene, can be mentioned.

[0043] Ethylene and annular olefin random copolymer (i) You may usually contain less than [20 mol %] and two or more sorts of units which may contain in the amount not more than 10 mol % preferably, and are drawn from other monomers for the unit drawn from other above monomers.

[0044] The above ethylene and annular olefin random copolymers (i) It can manufacture by the manufacture method indicated by the above-mentioned official report using the annular olefin shown by ethylene, the formula [I], or [II]. It is desirable to manufacture ethylene and an annular olefin random copolymer using the catalyst which performs this copolymerization in a hydrocarbon solvent and is formed in this hydrocarbon solvent from the vanadium compound and organoaluminium compound of fusibility as a catalyst also among these.

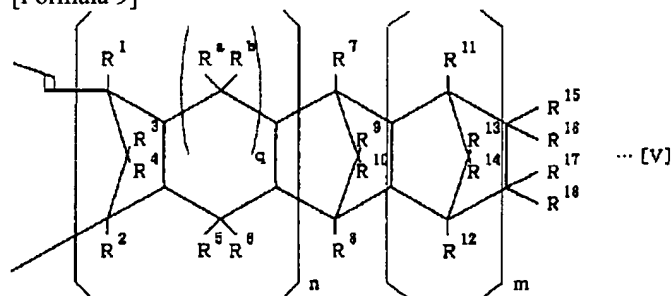
[0045] Moreover, at this copolymerization reaction, a solid-state-like IVB group metallocene system catalyst can also be used. A solid-state-like IVB group metallocene system catalyst is a catalyst which consists of the transition-metals compound containing the ligand which has a cyclopentadienyl skeleton, an organic aluminum oxy compound, and an organoaluminium compound blended by the need here. As an IVB group's transition metals, it is a zirconium, titanium, or a hafnium and these transition metals have the ligand containing at least one cyclopentadienyl skeleton here. Here, the cyclopentadienyl group which the alkyl group may replace as an example of the ligand containing a cyclopentadienyl skeleton or an indenyl group, a tetrahydro indenyl group, and a FUROORENIRU machine can be mentioned. These bases may be combined through other bases, such as an alkylene machine. Moreover, ligands other than the ligand containing a cyclopentadienyl skeleton are an alkyl group, a cycloalkyl machine, an aryl group, an aralkyl machine, etc.

[0046] Furthermore, what is usually used for manufacture of an olefin system resin can be used for an organic aluminum oxy compound and an organoaluminium compound. Such a solid-state-like IVB group metallocene system catalyst is indicated by JP,61-221206,A, 64-106, JP,1-173112,A, etc.

[0047] It is thought that a part of annular olefin [at least] shown by the above-mentioned formula [I] or [II] constitutes the repeat unit shown by the following formula [V] or [VI] from the ring-opening-polymerization object or ring breakage copolymer of (ii) annular olefin used by this invention.

[0048]

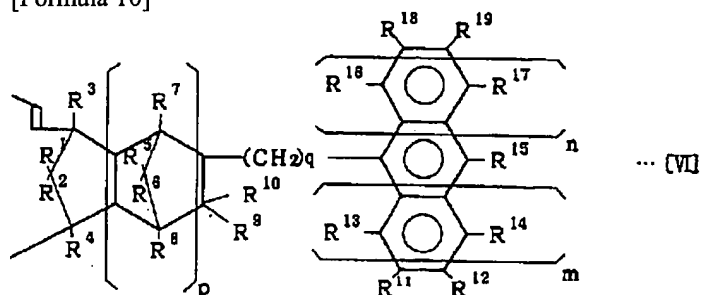
[Formula 9]



[0049] (In a formula [III], Ra and Rb are the same meanings as the same sign in a formula [I] at n, m, q, R1 - R18 row.)

[0050]

[Formula 10]



[0051] (In a formula [IV], n, m, p, q, and R1 -R19 are the same meanings as the same sign in a formula [II].)

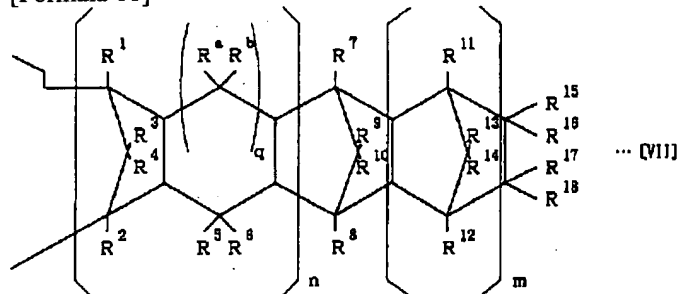
The annular olefin which can manufacture the above ring breakage (**) polymers (ii) by the manufacture method indicated by the aforementioned official report, for example, is expressed with the above-mentioned formula [I] can be manufactured a polymerization or by carrying out copolymerization under existence of a ring-opening-polymerization catalyst.

[0052] The catalyst which consists of the metaled halogenide or acetylaceton compound chosen from the catalyst which consists of the halogenide of the metal chosen from a ruthenium, a rhodium, palladium, an osmium, an indium, or platinum, a nitrate or an acetylaceton compound, and a reducing agent as a ring-opening-polymerization catalyst or titanium, palladium, a zirconium, or molybdenum, and an organoaluminium compound can be used.

[0053] (iii) The hydride of a ring breakage (**) polymer hydrogenates above ring-opening-polymerization objects or ring breakage copolymers (ii) under existence of well-known catalysts for hydrogenation conventionally, and is obtained. hydride (iii) of this ring breakage (**) polymer **** -- it is thought that a part of unit [at least] drawn from a formula [I] or [II] is expressed with the following formula [VII] or [VIII]

[0054]

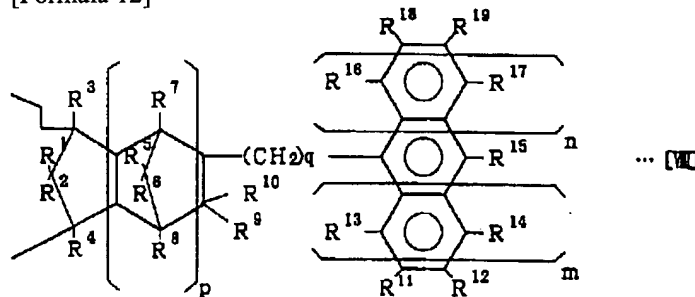
[Formula 11]



[0055] (In a formula [VII], Ra and Rb are the same meanings as the same sign in a formula [I] at n, m, q and R1 - R18 row.)

[0056]

[Formula 12]



[0057] (In a formula [VIII], n, m, p, q, and R1 -R19 are the same meanings as the same sign in a formula [II].)

(iv) -- the ethylene and annular olefin random copolymer of the above [the graft denaturation object of an annular olefin system resin] (i) Graft denaturation object (iii) of the hydride of the ring-opening-polymerization object of an annular olefin, a copolymer (ii), or a ring breakage (**) polymer it is .

[0058] As this modifier ** -- usually -- an unsaturation carvone -- acids use -- having -- concrete (meta) -- acrylic-acid, maleic-acid, fumaric-acid, tetrahydrophthal acid, itaconic-acid, citraconic-acid, crotonic-acid, isocrotonic-acid, and endo-cis-bicyclo -- [2.2.1] Hept-5- unsaturated carboxylic acids, such as an en -2 and 3-dicarboxylic acid (NAJIKKU acid TM), -- the derivative of these unsaturated carboxylic acids, for example, an unsaturation carvone acid anhydride, unsaturated-carboxylic-acid halide, an unsaturation carvone acid amide, an unsaturation carvone acid imide, the ester compound of a unsaturated carboxylic acid, etc. are As a derivative of a unsaturated carboxylic acid, maleic-anhydride, anhydrous citraconic-acid, and chlorination MARENIRU, maleimide, maleic-acid monomethyl, a maleic-acid dimethyl, glycidil maleate, etc. are mentioned more concretely.

[0059] these modifiers -- the anhydride of alpha and beta-unsaturation dicarboxylic-acid and alpha, and beta-unsaturation dicarboxylic-acid anhydride, for example, a maleic acid, a NAJIKKU acid, and these acids is used preferably also in inside Two or more sorts of these modifiers can be combined, and they can also be used.

[0060] As for the rate of denaturation in the graft denaturation object of the annular olefin system resin used by this invention, it is desirable that it is usually less than [10 mol %]. Such a graft denaturation object of an annular olefin system resin can blend and carry out the graft polymerization of the modifier to an annular olefin system resin, can also be manufactured so that it may become a desired rate of denaturation, can prepare the denaturation object of the rate of high denaturation beforehand, and can also manufacture it by subsequently mixing this denaturation object and the annular olefin system resin of native.

[0061] In order to obtain the graft denaturation object of an annular olefin system resin from an annular olefin system resin and a modifier, the denaturation method of well-known polymer is widely applicable conventionally. For example, a graft denaturation object can be obtained by the method of adding and carrying out the graft polymerization (reaction) of the modifier to the

annular olefin system resin in a melting state, or the method of adding a modifier in the solvent solution of an annular olefin system resin, and carrying out a graft reaction.

[0062] Such a graft reaction is usually performed at the temperature of 60-350 degrees C. Moreover, a graft reaction can be performed to the bottom of coexistence of radical initiators, such as organic peroxide and an azo compound.

[0063] Moreover, the above denaturation objects of the rate of denaturation can also be obtained by diluting so that it may become the rate of denaturation of a request of this denaturation object with the annular olefin system resin of native, after being able to obtain directly by the graft reaction of an annular olefin system resin and a modifier and obtaining the denaturation object of the rate of high denaturation beforehand by the graft reaction of an annular olefin system resin and a modifier.

[0064] The (i) above as an annular olefin system resin in this invention Either (ii) and (iii) (iv) may be used, and you may use combining these. Also among these, they are ethylene and an annular olefin random copolymer (i). It is used especially preferably.

[0065] In this invention, the annular olefin system resin Plastic solid processed by steam or hot water is obtained by fabricating the above annular olefin system resins by methods, such as an injection-blow-molding method, well-known forming method, for example, injection-molding method, a direct-blow-molding method, a T die method, a tubular film process, and the pressing method.

[0066] The configuration of a Plastic solid is not limited especially that what is necessary is just a request configuration according to the purposes of use, such as the shape of the shape of the shape of a container, and a tray, the shape of a sheet, and a film. As long as this annular olefin system resin Plastic solid is a range which does not spoil the purpose of this invention, it may contain other components arbitrarily. As other components, stabilizers, such as a heat-resistant stabilizer and a weathering stabilizer, a cross linking agent, a bridge formation assistant, an antistatic agent, a slipping agent, an anti blocking agent, an antifogger, lubricant, a color, a pigment, a straight-mineral-oil system softener, a petroleum resin, a wax, etc. can also be used.

[0067] As the stabilizer contained as this arbitrary component For example, fatty-acid metal salts, such as a phenol system antioxidant [, such as tetrakis [methylene-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate] methane, beta-(3, 5-G t-butyl-4-hydroxyphenyl) propionic-acid alkyl ester, 2, and 2'-OGIZAMIDOBISU [ethyl-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate,], zinc-stearate, calcium-stearate, 1, and 2-hydroxy calcium stearate, These can also be combined and used, for example, can also be used combining tetrakis [methylene-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate] methane, a zinc stearate, or a calcium stearate.

[0068] Moreover, it is a stabilizer. For example, distearyl pentaerythritol diphosphite, JI (nonylphenyl) pentaerythritol diphosphite, A phenyl -4, 4'-isopropylidene diphenol-pentaerythritol diphosphite, Bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, Screw (2, 6-G t-butyl-4-methylphenyl) pentaerythritol diphosphite, Phenyl bisphenol-A-pentaerythritol diphosphite, A tris (2, 4-G t-buthylphenyl) force fight, a tris (nonylphenyl) force fight, The Lynn system stabilizers, such as tetrakis (2, 4-G t-buthylphenyl) -4, 4'-biphenylene diphosphite, and screw (2, 6-G t-butyl-4-methylphenyl) pentaerythritol diphosphite, are mentioned.

[0069] Moreover, the fatty acid ester of polyhydric alcohol can be used as other components. As this polyhydric alcohol, the polyhydric alcohol more than trivalent, for example, a glycerol, a pentaerythritol, etc. are mentioned. Moreover, as a fatty acid, the aliphatic monocarboxylic acid of carbon numbers 5-20 is mentioned, for example, a lauric acid, a myristic acid, a palmitic acid, stearin acid, etc. are mentioned. Among these, the partial ester of polyhydric alcohol is then used preferably. The fatty acid ester of pentaerythritols, such as glycerine fatty acid esters, such as glycerine monolaurate, a glycerol monochrome millimeter state, glycerol monopalmitate, glycerol monostearate, glycerol dilaurate, and glycerol distearate, pentaerythritol monochrome laurate, pentaerythritol monostearate, pentaerythritol dilaurate, pentaerythritol distearate, and pentaerythritol tristearate, is used preferably concretely.

[0070] Moreover, an annular olefin system resin is even if it is the range which does not spoil the purpose of this invention and contains the organic filler or the inorganic filler. It may be good, for example, a silica, diatomaceous earth, an alumina, titanium oxide, a magnesium oxide, a pumice powder, a pumice balloon, an aluminum hydroxide, a magnesium hydroxide, a basic magnesium carbonate, a dolomite, a calcium sulfate, a potassium titanate, a barium sulfate, a calcium sulfite, talc, clay, a mica, asbestos, glass flakes, a glass bead, a calcium silicate, a montmorillonite, a bentonite, graphite, the aluminium powder, the molybdenum sulfide, etc. may be contained. The annular olefin system resin Plastic solid may contain two or more sorts of other components.

[0071] In steam processing of a Plastic solid, or a hot water art this invention, above hot water processings or steam processings of an annular olefin system resin Plastic solid are performed as follows. Hot water processing or steam processing of a Plastic solid is performed by being carried out under the sterilization processing conditions by the sterilization using usual hot water or usual steam, for example, contacting the hot shape of a gas and hot liquefied water to this Plastic solid by methods, such as sterilization by high pressure steam, such as the autoclave method and the steam method, and boiling method. The steam at the time of sterilization processing or the temperature (T degrees C) of hot water is usually 80 degrees C or more, and the processing time is usually more than for 5 minutes.

[0072] the time (T-50) of making processing temperature by hot water or steam into T degrees C in this invention immediately after processing by above-mentioned hot water or above-mentioned steam -- temperature higher than ** -- more than ** (T-30), it is the temperature more than ** (T-20) still more preferably, and holds more than for 20 minutes preferably more than for 10 minutes in 20% or less of atmosphere preferably [50% or less of relative humidity] In addition, the upper limit of this retention temperature should just be temperature which does not spoil the configuration of a Plastic solid. Thus, in case it moves in the hot blast oven held at the above-mentioned atmosphere and holds after carrying out the steam sterilization of the Plastic solid for

example, within an autoclave, it is desirable to move the Plastic solid after steam processing in oven promptly.

[0073] Thus, by holding in the above-mentioned atmosphere immediately after hot water processing or steam processing, the milkiness (cloudiness) by hot water processing or steam processing of an annular olefin system resin Plastic solid can be prevented.

[0074] According to such this invention, even if it performs sterilization processing to an annular olefin system resin Plastic solid, the transparency of this Plastic solid and appearance are not spoiled. Moreover, in this invention, since a white blush mark can be prevented as mentioned above even if an annular olefin system resin Plastic solid has not contained the additive for milkiness prevention, it is suitably used as medical devices, such as drug containers, such as physic tools, for example, a vial bottle, by which especially steam sterilization is carried out, a tablet bottle, a prefilled syringe, a test tube, and a petri dish, a dialyzer, and a waste blood tank, or a food container by which hot water processing is carried out.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the steam or the hot water art of the above annular olefin system resin Plastic solids, sterilization processing of the annular olefin system resin Plastic solid can be carried out by steam or hot water, without producing a white blush mark.

[Translation done.]

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EXAMPLE

[Example] Next, although an example explains this invention concretely, this invention is not limited to these examples. In addition, it set to this invention, and the following method measured or estimated various physical properties.

[0077] (1) Softening temperature temperature (TMA)

Du Pont make It measured by the heat deformation behavior of a sheet with a thickness of 1mm using Thermal Mechanical Analyzer. The needle made from a quartz was put on the sheet, 49g of loads was applied, the temperature up was carried out the speed for 5-degree-C/, and temperature at which the needle invaded 0.635mm into the sheet was set to TMA.

(2) Glass transition temperature (Tg)

the product made from SEIKO Electronic industry -- it measured by part for 10 degrees-C/of programming rates using DSC-20

(3) a light transmission and Hayes -- respectively -- ASTM It measured based on D1003.

[0078]

[Example 1] Softening temperature temperature (TMA) was 155 degrees C (Tg=144 degree C), and MFR (260 degrees C, measurement under a condition which is 2160g) carried out injection molding of the ethylene norbornene copolymer for 10g / 10 minutes, and obtained the corner guard with a thickness of 2mm. Hayes of this corner guard is shown in Table 1.

[0079] The steam processing above-mentioned corner guard was put into the autoclave, and steam processing was carried out for 20 minutes at 121 degrees C. After the steam processing end, the corner guard was immediately taken out from the autoclave and it heated in the atmosphere of 5% of relative humidity in the hot blast oven set as 120 degrees C for 2 hours. Hayes of the corner guard after the above-mentioned processing is shown in Table 1.

[0080]

[The example 1 of comparison] The corner guard obtained by carrying out injection molding like an example 1 was left for 2 hours in 23 degrees C and the interior of a room of 50% of relative humidity, after carrying out steam processing for 20 minutes at 121 degrees C. Hayes of the corner guard after processing is shown in Table 1.

[0081]

[Table 1]

		実施例 1	比較例 1
ヘイズ (%)	スチーム処理前	1. 2	
	スチーム処理後	1. 2	3. 3

[Translation done.]